

(12) UK Patent Application (19) GB (11) 2 166 126 A

(43) Application published 30 Apr 1986

(21) Application No **8426974**

(22) Date of filing **25 Oct 1984**

(71) Applicant

**Mitsubishi Mining & Cement Co Ltd (Japan),
5-1 Marunouchi 1-chome, Chiyoda-ku, Tokyo, Japan**

(72) Inventors

**Yoshiharu Ozaki
Yoshinori Shinohara
Hisatsugu Yoshida**

(74) Agent and/or Address for Service

**Marks & Clerk,
57-60 Lincoln's Inn Fields, London WC2A 3LS**

(51) INT CL⁴

C01B 13/32 C01F 7/02 C01G 21/02 23/053 49/02

(52) Domestic classification

C1A N13 N24 N34 N40 N4 PD2D

(56) Documents cited

GB A 2131782	GB 1265005	EP A1 0018035
GB A 2070579	EP A1 0027334	
GB A 2023115	EP A1 0024900	

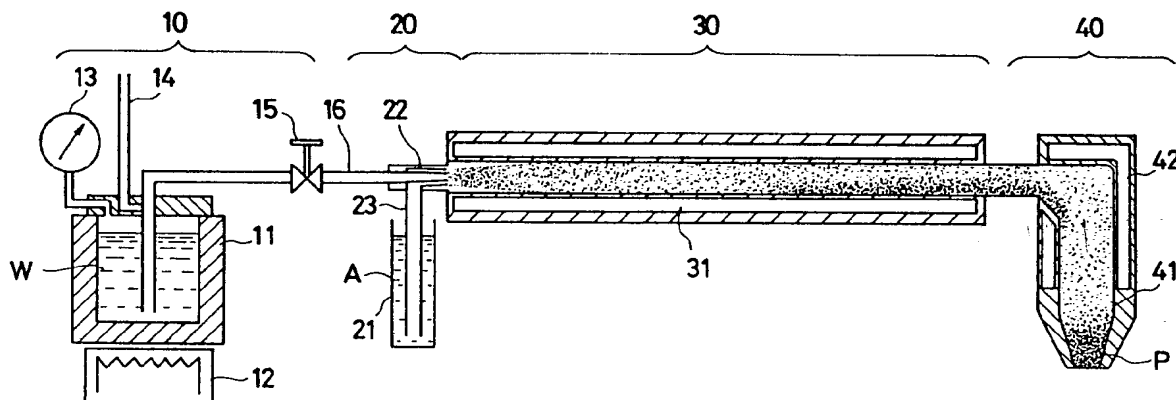
(58) Field of search

**C1A
C7F**

(54) Production of a ceramic powder

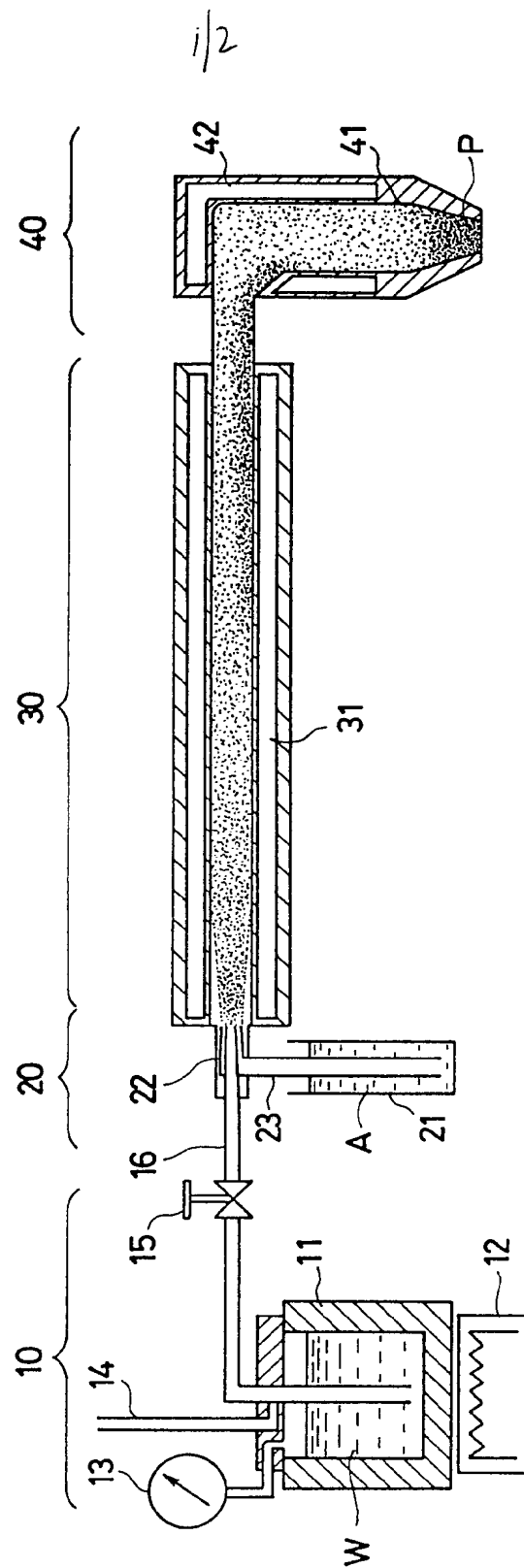
(57) Ceramic powder is manufactured by (a) spraying and hydrolyzing, in the presence of water, at least one substance which produces by such hydrolysis a metallic or non-metallic oxide, hydroxide or hydrate and (b) calcining the products. The ceramic powder may be prepared by an apparatus comprising a spray/hydrolysis section 20 which sprays and hydrolyzes under the presence of water the said at least one hydrolysable substance and a calcining section 30 which calcines the product of hydrolysis in the spray. The sprayed substances are thus completely hydrolyzed before thermal decomposition inside a furnace and immediately calcined to achieve a final ceramic powder product.

FIG. 1



GB 2 166 126 A

FIG. 1



2/2

FIG. 2

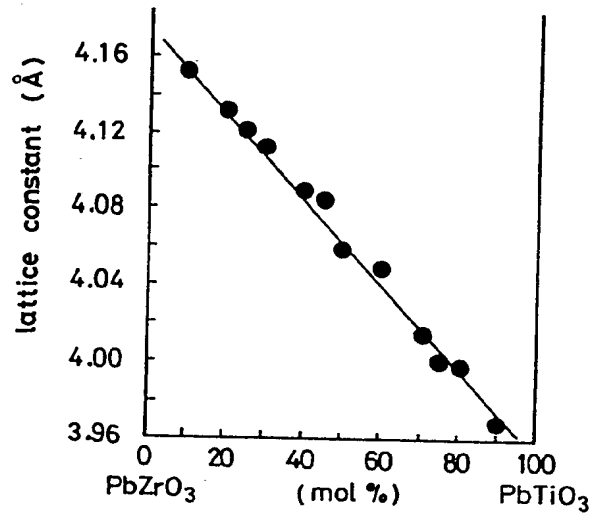
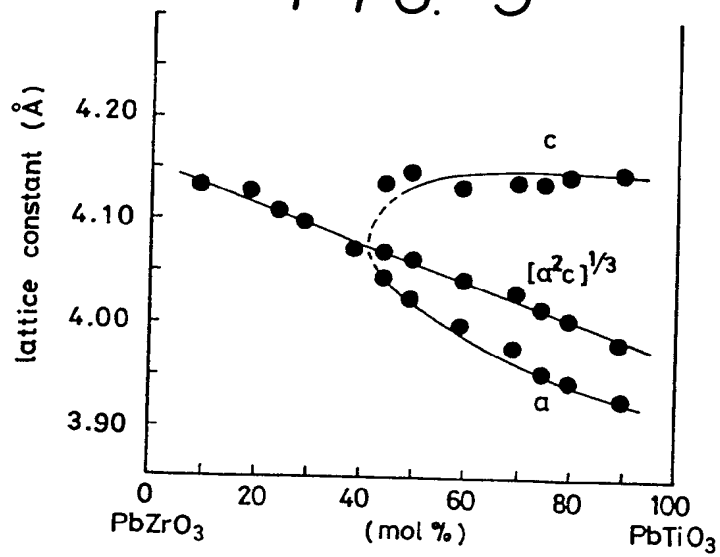


FIG. 3



SPECIFICATION

Production of ceramic powder

5 This invention relates to a method of preparing ceramic powder from the liquid phase and to an apparatus for this purpose. 5

Known methods for preparing ceramic powder from substances in a liquid phase, such as alkoxides (which form oxides, hydroxides or hydrates of metals or non-metals by hydrolysis) include flame spraying which involves thermal decomposition and hydrolysis which involves precipitation. 10

Flame spraying involves spraying alkoxide solution into a high-temperature atmosphere so as instantaneously to evaporate the solvent and simultaneously to thermally-decompose the alkoxide itself, thus obtaining oxide powder in a one-stage process. However, powder thus obtained tends to be particles cohering together, thus being inferior in sintering at a later stage. Also, high temperatures are required for thermal decomposition, so that low-temperature-type oxides cannot be produced. 15

Alkoxide hydrolysis involves obtaining fine oxide powder by a multistage procedure comprising decomposing metal alkoxide with water (into alcohol on the one hand, and oxide or hydrate, on the other) filtration, drying, calcination and milling. Although this method can give low-temperature-type oxide, which the flame spraying method cannot, it involves a large number of steps thus complicating plant operation. Also particles tend to cohere under normal drying conditions thus occasionally necessitating further milling. Moreover, particle growth occurs during calcination and this also increases the tendency to cohere and consequent difficulty in obtaining a fine powder. The milling step tends moreover to introduce as impurities into the fine powder abrasive powder from the ball mills used. 25

The present inventors have observed and realised that alkoxide hydrolysis itself can be completed in an extremely short time. This invention is based on this observation and aims at providing a method of preparing a ceramic powder of small particle size, of high purity, in a short time and by a smaller number of processing steps.

30 The invention consists in a method of preparing a ceramic powder comprising the steps of (a) spraying and hydrolyzing, in the presence of water at least one substance which produces upon hydrolysis a metallic or non-metallic oxide, hydroxide or hydrate and (b) calcining the at least one metallic or non-metallic oxide produced hydroxides or hydrate of said substances produced in the as-sprayed condition. 35

In another aspect the invention consists in an apparatus for preparing ceramic powder comprising a spray/hydrolysis section provided with (a) a water-supplying nozzle which sprays and hydrolyzes at least one substance which produces by hydrolysis a metallic or non-metallic oxide, hydroxide or hydrate and (b) a calcining section connected directly to the spray section which calcines the metallic or non-metallic oxide, hydroxide or hydrate or each as formed by said hydrolysis while they are being sprayed. 40

Alkoxide, metal acetylacetonate or alkyl metal may be used in this invention by way of example of the substances which produce by hydrolysis metallic or non-metallic oxides, hydroxides or hydrates. Alkoxide is the most preferable as it undergoes relatively fast hydrolysis under spray conditions, and is easy to handle. Two or more kinds of alkoxides may be used jointly to obtain a fine powder of multiple oxides. The term "alkoxide" used herein means a compound obtained by substituting the hydrogen atom of the OH group in an alcohol with a metal atom. 45

Said substance may be sprayed in the presence of water for example (1) spraying a solution of the substance together with pressurized water or (2) contacting a solution of the substance a vapor or mist of water.

50 For the spraying, a two path nozzle, a rotary atomizer, a pressure nozzle, may be used. It is possible to spray water either from the same nozzle as the solution of the substance or from a separate nozzle. If the water is at a high temperature, a different form of final ceramic powder may be obtained by control of the calcination temperature, as will be described hereinafter. Spraying may be conducted by spraying the substances directly into a calcination furnace as will also be described hereinbelow. 55

Hydrolysis of the substance sprayed into such a furnace is complete before it is thermally decomposed by the heating and calcination.

A heating furnace to constitute the calcining section maybe connected to the spray nozzle so as to completely take in all hydrolysis products sprayed by the nozzle. It can be a sealed structure on the side of the nozzle. The calcining section should preferably have an elongated shape in dependence on the designed flow rate so that the oxides can be uniformly heated for calcination. The pressure inside the furnace, when it is sealed, is usually normal atmospheric pressure or higher. It is preferable to construct the calcination section so as to be adjustable in calcining temperature whereby control of the crystal structure of the ceramic powder product may be achieved. The calcining temperature may be selected depending on the end use of the 65

ceramic powder. For instance, it can be within the temperature range of 100°C to 1200°C or higher; the upper limit of the calcining temperature should be below the temperature at which decomposition of metallic or non-metallic oxides, hydroxides or hydrates sets in. A collecting filter is preferably provided in connection with the calcining section to facilitate recovery of ceramic powder. The ceramic powder, hot from the calcining process, may be cooled at the terminal end of the calcining section or at the collecting filter by any suitable cooling device provided therein.

Chemical analysis of the ceramic powder produced by the said calcining process reveals that the powder is typically of uniform size particles of high purity having 0.1% or less impurities. Where the starting material was a mixture of two or more components it was found that each particle has the same relative composition.

Thus, the invention enables preparation and manufacture of pure fine ceramic powder in a short time directly after hydrolysis by a simple process which does not need the thermal decomposition reactions of the prior art nor the various separate steps of filtration, drying or milling.

The invention will be further described with reference to the accompanying drawings, in which:-

Figure 1 is a diagrammatic section along one embodiment of apparatus which can be used according to the invention;

Figure 2 is a graph to show lattice constant changes of PZT powder calcined at 600°C according to the present invention method; and

Figure 3 is a graph to show lattice constant changes of PZT powder calcined at 1,000°C according to the present invention method.

The apparatus comprises a high-temperature/high-pressure water supply section 10, a spray/hydrolysis section 20, a calcining section 30 and a powder collecting section 40.

The high temperature/high pressure water supply section 10 comprises a pressure vessel or autoclave heated by a heater 12 to provide high temperature/high pressure water, a pressure as shown on gauge 13 and a thermometer 14. Valve 15 adjusts the flow rate and pressure of the high temperature/high pressure water W passing from the vessel 11 into pipe 16. For example the high temperature/high-pressure water supply can provide water at 260°C, 150Kg/cm², and valve 15 can adjust this to 70 Kg/cm² at 80°C.

The spray/hydrolysis section 20 comprises a container 21 which contains the alkoxide solution A which is to be hydrolysed to form oxide. From within the container 21 a vertical pipe 23 extends to the spraying mouth of the spray nozzle 22 which is connected at the free end of said pipe 16. This mixes the high temperature/high pressure water W with the alkoxide solution A.

The calcining section 30 is connected directly to the spray/hydrolysis section 20. It comprises a cylindrical furnace 31 which surrounds the spraying path of the nozzle 22 and extends in an elongated shape in dependence upon the designed spraying rate, as can readily be calculated or otherwise established by a man skilled in the art. The furnace temperature is controlled by a control device (not shown).

The powder collecting section 40 is provided next to the calcining section 30. It comprises a collecting filter 41 surrounded by a cooling device 42.

The use of the above equipment for preparing ceramic powder will now be explained.

A single alkoxide such as lead isopropoxide (Pb(OPr)₃), aluminum isopropoxide (Al(OPr)₃), iron ethoxide (Fe(OEt)₃), titanium isopropoxide (Ti(OPr)₄), or zirconium butoxide (Zr(OBu)₄); or a mixture of two or more of such alkoxides, e.g. Pb(OPr)₂ and Ti(OPr)₄; Pb(OPr)₂ and Zr(OBu)₄; Pb(OPr)₂, Ti(OPr)₄ and Zr(OBu)₄ may be used as starting material. This starting material is dissolved in benzene to a concentration of 0.1 mol/l. The alkoxide/benzene solution A is then fed from the pipe 23, and, by adjusting the valve 15, the high temperature/high pressure water W is supplied under a pressure of 70 Kg/cm². Both the water and the alkoxide solution are therefore sprayed from the nozzle 22 simultaneously. The alkoxide or mixture thereof, when sprayed from the nozzle 22 is hydrolyzed in its atomized condition; is immediately calcined in the furnace 31; and is collected by the filter 41 as ceramic powder P.

The temperature of the furnace 31 was varied at 600°C, 800°C, 1000°C and 1200°C to obtain oxide powders of different crystal systems. The table shows results of x-ray diffraction of the powder produced.

The table shows that as far as PZT powder was concerned a powder of the cubic system of high temperature stability was obtained at 600°C and 800°C. In the prior art method which involves calcination of alkoxide and water, a powder of low temperature stability and having a rhombohedral or tetragonal system was produced.

Table

	Furnace Temperature			
	600°C	800°C	1000°C	1200°C
$\text{Pb}(\text{OPr}^{\text{i}})_2$	PbO (Massicot type)	PbO (Massicot type)	PbO (Massicot type)	PbO (Massicot type)
$\text{Al}(\text{OPr}^{\text{i}})_3$	$\gamma\text{-Al}_2\text{O}_3$	$\delta\text{-Al}_2\text{O}_3$	$\theta\text{-Al}_2\text{O}_3$	$\alpha\text{-Al}_2\text{O}_3$
$\text{Fe}(\text{OEt})_3$	$\alpha\text{-Fe}_2\text{O}_3$	$\alpha\text{-Fe}_2\text{O}_3$	$\alpha\text{-Fe}_2\text{O}_3$	$\alpha\text{-Fe}_2\text{O}_3$
$\text{Ti}(\text{OPr}^{\text{i}})_4$	TiO_2 (anatase type)	TiO_2 (rutile type)	TiO_2 (rutile type)	TiO_2 (rutile type)
$\text{Zr}(\text{OBu}^{\text{n}})_4$	ZrO_2 (tetragonal system)	ZrO_2 (tetragonal system + orthorhombic system)	ZrO_2 (orthorhombic system)	ZrO_2 (orthorhombic system)
$\text{Pb}(\text{OPr}^{\text{i}})_2 + \text{Ti}(\text{OPr}^{\text{i}})_4$	PbTiO_3 (tetragonal system)	PbTiO_3 (tetragonal system)	PbTiO_3 (tetragonal system)	PbTiO_3 (tetragonal system)
$\text{Pb}(\text{OPr}^{\text{i}})_2 + \text{Zr}(\text{OBu}^{\text{n}})_4$	PbZrO_3 (cubic system)	PbZrO_3 (cubic system)	PbZrO_3 (orthorhombic system)	PbZrO_3 (orthorhombic system)
$\text{Pb}(\text{OPr}^{\text{i}})_2 + \text{Ti}(\text{OPr}^{\text{i}})_4 + \text{Zr}(\text{OBu}^{\text{n}})_4$	*PZT (cubic system)	PZT (cubic system)	PZT (rhombohedral/tetragonal system)	PZT (rhombohedral/tetragonal system)

* PZT herein means a solid solution the formula of which can be expressed as $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ where x is not greater than 1, and which thus has a composition intermediate between PbZrO_3 and PbTiO_3 .

Fig. 2 shows the lattice constant change calculated from x-ray diffraction patterns of various PZT powder compositions calcined at 600°C having different mole ratios of PbTiO_3 against PbZrO_3 . In the graph, PZT composition expressed in mole ratio is plotted on the lateral axis while the lattice constants calculated from x-ray diffraction patterns are plotted on the vertical axis. The powder calcinated at 800°C showed similar results to the powder calcined at 600°C.

Fig. 3 shows the lattice constant changes of each PZT powders calcined at 1000°C. The curves in the graph reveal that the powder had a rhombohedral system when PbZrO_3 was 10 to 40 mol% and a tetragonal system when it was 40 to 90 mol%. The powder calcined at 1,200°C showed similar results to the powder calcined at 1,000°C.

The particle size of all the powders obtained was observed by an electron microscope, which indicated the particle size was 0.04 μm at a calcination temperature of 600°C, and 0.08 μm at a temperature of 1,000°C. The powder obtained was in the form of extremely fine particles.

CLAIMS

1. A method of preparing a ceramic powder comprising the steps of (a) spraying and hydrolyzing, in the presence of water at least one substance which produces upon hydrolysis a metallic or non-metallic oxide, hydroxide or hydrate and (b) calcining the at least one metallic or non-metallic oxide produced hydroxides or hydrate of said substances in the as-sprayed condition.
2. The method of preparing ceramic powder as claimed in Claim 1 wherein one or more alkoxides are sprayed and hydrolysed.
3. The method of preparing ceramic powder as claimed in Claim 1 or 2 wherein spraying is conducted by spraying a solution of the or each such substance with pressurized water.
4. The method of preparing ceramic powder as claimed in Claim 1 or 2 wherein spraying is conducted by contacting the or each such substance with water in the form of vapor or mist.
5. The method of preparing ceramic powder as claimed in any one of Claims 1 to 4 wherein calcination is conducted at a temperature higher than 100°C but lower than the temperature of decomposition of the or each metallic or non-metallic oxide, hydroxide or hydrate.
6. An apparatus for preparing ceramic powder comprising a spray/hydrolysis section provided with (a) a water-supplying nozzle which sprays and hydrolyzes at least one substance which produces by hydrolysis a metallic or non-metallic oxide, hydroxide or hydrate and (b) a calcining section connected directly to the spray section which calcines the metallic or non-metallic oxide, hydroxide or hydrate or each as formed by said hydrolysis while they are being sprayed.
7. The apparatus as claimed in Claim 6 wherein the said calcining section is connection to the nozzle.
8. The apparatus as claimed in Claim 6 or 7 wherein the calcining section is of an elongated shape in dependence with the designed flow rate of the nozzle.
9. The apparatus as claimed in any one of Claims 6 to 8 wherein the calcining section is adapted for adjustment of the calcining temperature.
10. The apparatus as claimed in any one of Claims 7 to 9 wherein the calcining section is provided with a collecting filter.
11. The apparatus as claimed in Claim 10 wherein the collecting filter has a cooling device connected thereto.